Copy of conference proceedings for:

D.S.A. De Focatiis, C.P. Buckley and L.R. Hutchings (2007), *Environmental Stress Crazing in Polystyrene: the Roles of Chain Length and Architecture in Craze Initiation*, In: 65th Annual Technical Conference of the Society of Plastics Engineers 2007, 6-10 May 2007, Cincinnati, Ohio, pp. 3103-3107.

Note: the conference paper/abstract is provided for information in the following pages, but is more extensively described and published in the following journal publications, which can also be obtained from my website at http://www.nottingham.ac.uk/~enzddf . Please ensure you cite the relevant journal articles and not the conference papers.

Main journal articles relating to this conference paper:

D.S.A. De Focatiis, C.P. Buckley and L.R.Hutchings (2008), *Roles of Chain Length, Architecture and Time in the Initiation of Visible Crazes in Polystyrene*, Macromolecules 41(12) pp. 4484-4491. doi: 10.1021/ma702157m

D.S.A. De Focatiis and C.P. Buckley (2008), *Determination of Craze Initiation Stress in Very Small Polymer Samples*, Polymer Testing, 27 (2) pp. 136-145. doi: 10.1016/j.polymertesting.2007.08.006

Other relevant articles:

D.S.A. De Focatiis and C.P. Buckley (2011), *Craze initiation in glassy polymers: quantifying the influence of molecular orientation*, Polymer, 52 (18), pp 4045-4053. doi: 10.1016/j.polymer.2011.06.044

davide.defocatiis@nottingham.ac.uk

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation

Davide S.A. De Focatiis[†], C. Paul Buckley[†] and Lian R. Hutchings[‡]

[†]Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, UK [‡]IRC in Polymer Science and Technology, Department of Chemistry, University of Durham, Durham DH1 3LE, UK

Abstract

This work aims to assist in optimising the solid state performance of polymer products, by developing an understanding of the molecular factors involved in initiation of environmental stress crazing. Experiments measuring craze initiation stress in miniature rectangular beam samples saturated in diethylene glycol were performed on 26 isotropic atactic polystyrenes with molar mass from 66 kD to 1148 kD, including a wide range of monodisperse linear and branched materials. Results indicate that both solid-state molecular disentanglement and chain scission play roles, depending on the chain architecture and length of the polymer. A simple rule is suggested for predicting ESC craze initiation in polydisperse polymers.

Introduction

Environmental Stress Crazing (ESC) is a common cause of failure of glassy polymer products in contact with environmental agents. Crazing is a local deformation phenomenon of glassy polymers resulting from the application of a tensile stress over time. Crazes appear as long, thin highly deformed wedges of polymer, normal to the maximum principal stress, in which voiding occurs and highly drawn fibrils span the gap between the craze surfaces. There has been substantial research in the past 4 decades on the subject of craze initiation, and comprehensive reviews are available [1, 2]. Although there is still debate over the exact mechanisms taking place during craze initiation, there is agreement that a "geometrically necessary entanglement loss" must take place, as noted by Kramer [1].

Entanglement loss can come about as a result of solid-state molecular disentanglement if favorable conditions are present, such as high temperature, the presence of solvents, etc. [3]. Chain length must play a key role if disentanglement is to take place. When chain mobility is reduced, such as in dry crazing or at low temperatures, crazing occurs through chain scission [4], and the craze initiation stress is then expected to be independent of molar mass.

The objective of the present work is to develop an understanding of the effects of molecular parameters such as length, architecture and length distribution on the solid-state mechanical properties of polymers. In this paper we report measurements of the craze initiation stress in isochronal 3-point bending creep experiments on a wide variety of well-characterized grades of atactic polystyrene (PS) and put forward a simple model that relates molecular parameters to craze initiation. A novel miniature crazing test was employed, to enable study of materials where only small quantities are available.

Materials and Methods

Materials

The materials used in this study were atactic polystyrenes including a wide range of monodisperse linear PS (PDI = $M_w/M_n < 1.15$), a selection of monodisperse 3 and 4-arm star PS [5], and several linear polydisperse PS. Molar mass measurements performed by GPC are shown in Table 1.

Experimental method

PS plates 0.5mm in thickness were compression moulded using rectangular moulds in a hand-operated hydraulic press with heated platens. The top and bottom surfaces of the mould were lined each time with a fresh sheet of 0.15 mm thick aluminium foil, in order to provide a repeatable surface roughness. The mould was held at 170°C for 15 minutes and cooled to room temperature at a rate of 15°C/min. Miniature rectangular beam samples typically 0.5 mm x 2 mm x 7 mm in size were cut from the plates using a custom-made jig with parallel single bevelled blades. Samples were soaked in diethylene glycol (DEG) for a minimum of 1 day prior to testing. No further solvent uptake could be measured after 1 day. A consequence of the presence of the solvent is to ensure the growth of fine crazes required in the miniature specimens and to avoid premature brittle fracture as seen frequently in specimens crazed in air.

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation, D.S.A. De Focatiis, C.P. Buckley and L.R. Hutchings, 2007. Crazes were induced in the miniature beams by subjecting them to 3-point bending at constant load for 300 s while immersed in DEG as shown in Figure 1. The long axes of the beams were always aligned parallel to the machine direction of the foil used during moulding. The width of the crazed region under the applied load was then measured within 1 hour of unloading, employing a low power optical microscope exploiting the reflective property of the crazes as shown in Figure 2.

Results

Elementary beam theory was employed to find the stress at the extremities of the crazed region, from the average of 5 measurements of the length of the crazed region, l_c , taken across the width of each sample

$$\sigma_{\rm c} = \frac{3P(L-l_{\rm c})}{2bt^2} \tag{1}$$

where *P* is the load applied, *L* is the support spacing, *b* the breadth and *t* the thickness of the beam.

It was not possible to generate stable crazes in the lowest molar mass PS, sample A. A number of authors have reported that it is not possible to grow stable crazes in monodisperse polymers of molecular weight close to $2M_e$ [6, 7], where the entanglement molecular weight M_e = 18 kD for PS [8, 9]. In crazing it is thought that molecules shorter than $2M_e$ are not coupled to the entanglement network and merely dilute it. For polymer A we instead established a lower bound for the stress at no craze formation and an upper bound for the stress at which unstable craze propagation leads to fracture.

A minimum of 4 samples were tested for each polymer, although more repetitions were performed where more material was available. The mean and standard deviations are shown in Table 1.

Discussion

In order to account for the dependence of craze initiation stress on chain length, we refer to the theory of Han *et al* [10] who point out that in order for chain disentanglement to take place at the craze tip there must be a mechanism of chain retraction. As a polymer chain is extended at the craze interface, its contour length increases, and it strives to retract within its "tube", destroying entanglements in the process and allowing the mature craze to form. At the craze tip the mobility of the polymer is enhanced through stress-activation and free surface. Once the polymer chain becomes part of a craze fibril it returns to the glassy state, and complete retraction is prevented. Han *et al* suggest that the disentanglement required for craze formation is such that the experiment time is of the order of the longest Rouse retraction time $\tau_{\rm R}$. $\tau_{\rm R}$ is linked to molar mass *M* through

$$\tau_{\rm R} = \tau_{\rm e} \left(\frac{M}{M_{\rm e}}\right)^2 \tag{2}$$

where $\tau_{\rm e}$ is the Rouse time of one entanglement length.

We consider the disentanglement event in craze initiation to be a stress-accelerated flow process that can be described by an equation of Eyring form

$$\tau = \tau_{\rm R} \exp\left(-\frac{\sigma_{\rm c} V_{\rm c}}{RT}\right) \tag{3}$$

where τ is the time for disentanglement by retraction when accelerated by far-field tensile stress σ_c , V_c is the associated activation volume, *R* is the gas constant and *T* is the temperature.

Assuming a given number of craze fibrils, and hence of disentanglements, is required for a craze to become visible within the experimental time-window *t*, it follows that for a visible craze $\tau \propto t$. Hence from equations (2) and (3), in the case of linear monodisperse chains long enough to be entangled ($M > M_e$), the stress for craze initiation by disentanglement is

$$\sigma_{\rm c}^{\rm dis} = a \log_{10} M + b \tag{4}$$

where *a* and *b* are constants for experiments of given duration, at a given temperature, on a given polymer.

In branched chains with a single branch point, the molar mass associated with chain retraction is the span molar mass M_s [9]. Where M_s is only a small number of entanglement lengths there may be differences between τ_R for a branched chain of M_s compared with a linear chain of length M_s since the branch point effectively pins the centre of mass of the chain. When the equivalent linear chain is long, the random nature of the fluctuations along the tube effectively pins its midpoint in the same way as a branch point. The shortest equivalent chain for the branched polymers used in this study is about 7 entanglements.

For each branched polymer in this study M_s is obtained from the nominal dimensions of the architecture, in preference to M_w that is influenced by the small number of abnormal branch points in the sample. The values used are given in Table 1.

Craze initiation data from linear and branched monodisperse samples are plotted against $\log M$ in Figure 3. Linear regression was used on measurements from linear samples B, C, D and branched sample AW to

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation, D.S.A. De Focatiis, C.P. Buckley and L.R. Hutchings, 2007. define the linear region of disentanglement crazing given by equation (4), giving parameters $a = 23\pm5$ MPa/log₁₀D and $b = -100\pm27$ MPa. Measurements from high molar mass samples where σ_c is independent of molecular weight were averaged to give the scission craze initiation stress $\sigma_c^{sci} = 17.6\pm2.1$ MPa. The transition from disentanglement to chain scission occurred at $M_{crit} \approx 160$ kD $\approx 9M_e$. Extrapolation of the linear region to zero craze initiation stress occurs at $M \approx 27$ kD which is close to $2M_e$.

For polydisperse chains we assume here that the mass fraction $\phi_{\rm dil}$ with $M < 2M_{\rm e}$ simply dilutes the mixture; in the mass fraction $\phi_{\rm dis}$ with $2M_{\rm e} < M < M_{\rm crit}$ each molecule contributes to the craze initiation stress through its retraction time; and in the remaining mass fraction $\phi_{\rm sci} = 1 - (\phi_{\rm dil} + \phi_{\rm dis})$ with $M > M_{\rm crit}$ there is a constant contribution through chain scission. Let $M_{\rm w}^{\rm dis}$ be the mass-averaged geometric mean molar mass for the mass fraction $\phi_{\rm dis}$ with $2M_{\rm e} < M < M_{\rm crit}$. Then adding the contributions from disentanglement and scission gives

$$\sigma_{\rm c} = \phi_{\rm dis} \left(a \log_{10} M_{\rm w}^{\rm dis} + b \right) + \phi_{\rm sci} \sigma_{\rm c}^{\rm sci} \tag{5}$$

Only polymer R has a significant number of chains shorter than $M_{\rm crit}$. The molar mass distribution for polymer R is shown in Figure 4. Computing the discrete distribution as obtained by GPC gives $\phi_{\rm dil} = 0.08$, $\phi_{\rm dis} =$ 0.39 and $\phi_{\rm sci} = 0.51$; $M_{\rm w}^{\rm dis} = 92.2$ kD; giving a predicted $\sigma_{\rm c} = 13.9$ MPa, which is close to, within measurement uncertainty, the measured value of 15.9 ± 1.2 MPa.

Conclusions

This study has investigated experimentally the effects of chain length and architecture on environmental craze initiation in polystyrene. The results indicate that in linear monodisperse PS there are two regions of behaviour: solid-state disentanglement for M < 160 kD and chain scission for M > 160 kD. In the disentanglement region the craze initiation stress is linearly related to logM; in the chain scission region it is independent of M.

Branched PS follows the same pattern of behaviour as linear PS provided that the span molecular weight M_s is used in place of M.

For linear polydisperse PS, the two contributions to craze initiation stress, arising from the portions of molar mass distribution above and below the disentanglement – chain scission transition, are weighted by mass and added. This agrees with experiment for the one polymer where it could be tested.

Acknowledgements

This work was supported by the UK Engineering and Physical Sciences Research Council grant number GR/T11845/01.

References

- Kramer, E.J., *Microscopic and molecular* fundamentals of crazing. Advances in Polymer Science, 1983. 52/53: p. 1-56.
- 2. Sauer, J.A. and M. Hara, *Effect of molecular variables on crazing and fatigue of polymers*. Advances in Polymer Science, 1990. **91/92**: p. 69-118.
- Donald, A.M., *The Effect of Temperature on Crazing* Mechanisms in Polystyrene. Journal of Materials Science, 1985. 20(7): p. 2630-2638.
- 4. Yang, A.C.M., E.J. Kramer, C.C. Kuo, and S.L. Phoenix, *Craze Fibril Stability and Breakdown in Polystyrene*. Macromolecules, 1986. **19**(7): p. 2010-2019.
- Clarke, N., F.R. Colley, S.A. Collins, L.R. Hutchings, and R.L. Thompson, *Self-diffusion and viscoelastic* measurements of polystyrene star polymers. Macromolecules, 2006. **39**(3): p. 1290-1296.
- 6. Yang, A.C.-M. and E.J. Kramer, *Craze Fibril Stability and Breakdown in Polystyrene*. Macromolecules, 1986. **19**: p. 2010-2019.
- McGarel, O.J. and R.P. Wool, *Craze Growth and Healing in Polystyrene*. Journal of Polymer Science: Part B: Polymer Physics, 1987. 25: p. 2541-2560.
- Mark, J.E., K.L. Ngai, W.W. Graessley, L. Mandelkern, E.T. Samulski, J.L. Koenig, and G.D. Wignall, *Physical properties of polymers*. 3rd ed. ed. 2003, Cambridge: Cambridge University Press.
- Han, H.Z.Y., R.A. Duckett, T.C.B. McLeish, N.J. Ward, and A.F. Johnson, *Drawing and orientation*relaxation behaviour of monodisperse linear and 3arm star polystyrenes. Polymer, 1997. 38(7): p. 1545-1555.
- 10. Han, H.Z.Y., T.C.B. McLeish, R.A. Duckett, N.J. Ward, and A.F. Johnson, *Experimental and Theoretical Studies of the Molecular Motions in Polymer Crazing. 1. Tube Model.* Macromolecules, 1998. **31**: p. 1348-1357.

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation, D.S.A. De Focatiis, C.P. Buckley and L.R. Hutchings, 2007.

Annual Technical Conference of the Society of Plastics Engineers (ANTEC 2007)
Cincinnati, Ohio, May 6-10 2007	

	Code	$M_{\rm w}$ (kD)	PDI	Architecture	Mean	SD	$M_{\rm s}({\rm kD})$
					σ _c (MPa)	σ _c (MPa)	
Linear monodisperse	Α	68.0	1.030	linear	- *	- *	
	В	75.5	1.029	linear	10.1	0.5	
	С	94.4	1.052	linear	12.0	1.1	
	D	108.4	1.044	linear	14.4	1.9	
	AX	132.9	1.045	linear	19.7	1.5	
	AY	148.1	1.059	linear	18.5	2.0	
	Е	160.8	1.033	linear	17.6	1.9	
	Р	206.3	1.084	linear	18.6	1.6	
	AZ	226.1	1.101	linear	19.2	1.5	
	F	249.3	1.122	linear	17.1	1.7	
	G	498.2	1.072	linear	15.8	2.3	
	BB	966.5	1.073	linear	16.7	0.9	
3-arm	AA	200.5	1.050	3-arm asym [†]	17.9	0.8	180
stars	Z	435.0	1.050	3-arm star	17.9	0.8	290
4-arm stars	AW	234.2	1.071	4-arm star	13.7	2.0	120
	AQ	440.6	1.070	4-arm star	17.6	2.3	200
	AR	541.3	1.057	4-arm star	18.2	0.9	267
	AS	821.3	1.030	4-arm star	17.7	1.2	400
	AT	1148.0	1.023	4-arm star	19.0	0.5	600
H-shape	AB	310.0	1.050	H-shape [‡]	18.0	1.5	
Linear polydisperse	R	217.7	2.536	linear polyd.	15.9	1.2	
	BA	221.4	1.260	linear polyd.	19.6	1.5	
	Ν	230.4	1.279	linear polyd.	17.5	1.6	
	Х	293.3	1.967	linear polyd.	18.8	1.4	
	W	518.8	2.845	linear polyd.	19.3	2.7	
	0	526.8	1.594	linear polyd.	18.7	0.8	

Table 1 - Polystyrene grades used in this study, with weight-average molecular weight M_{w} , polydispersity index PDI, mean craze initiation stress and its standard deviation.

Could not be crazed in a stable manner. Experiments suggest that crazes do not form at 8.1 MPa, and the sample undergoes brittle fracture at 10.5 MPa.

[†] Asymmetric star has nominally 2 arms 90 kD and 1 arm 20 kD. [‡] H-shape has nominally a central span 100 kD connected to 1 arm 35 kD and 1 arm 70 kD on both sides.

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation, <u>D.S.A. De Focatiis</u>, C.P. Buckley and L.R. Hutchings, 2007.

Annual Technical Conference of the Society of Plastics Engineers (ANTEC 2007) Cincinnati, Ohio, May 6-10 2007



Figure 1 - The miniature 3-point bending creep crazing test.



Figure 3 - 300s craze initiation stress results for linear (M) and branched (M_s) monodisperse PS.



Figure 2 - The use of the reflective property of crazes to measure the width of the crazed region.



Figure 4 - Molar mass distribution from GPC for polymer R in arbitrary units showing the position of $M_{\rm crit}$.

Environmental stress crazing in polystyrene: the roles of chain length and architecture in craze initiation, <u>D.S.A. De Focatiis,</u> C.P. Buckley and L.R. Hutchings, 2007.